THE DIELECTRIC BEHAVIOUR OF MONOCATIONIC MONTMORILLONITES

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Na,Ca–,Na– AND Ca–MONTMORILLONITES WERE USED AS DIELECTRICS IN A SEARCH FOR A RELATION BETWEEN THE ABILITY TO SWELL, X–RAY DIFFRACTION RESULTS AND DIELECTRIC PROPERTIES. THE CAPACITY AND CONDUCTIVITY OF MONTMORILLONITE TABLETS PLACED BETWEEN MINIATURE CONDENSING BLADES WERE MEASURED AS A FUNCTION OF TEMPERATURE, WHICH WAS VARIED VIA CONSTANT FREQUENCIES OF AN AC BRIDGE. THE PERMITTIVITY WAS DETERMINED FROM THE MEASURED CAPACITANCE. IT WAS FOUND THAT THE BEHAVIOUR OF THE SAMPLES WAS INFLUENCED PRIMARILY BY THE NATURE OF THE EXCHANGEABLE CATIONS AND BY THEIR MADE OF CONNECTION TO THE MONTMORILLONITE SHEET, AND SECONDLY BY THE PRESENCE AND NATURE OF THE ANIONS FORMING AN ELECTRIC DOUBLE LAYER ON THE OUTSIDE ARMATURE ON THE EDGES OF THE CLAY PARTICLES. IN FACT, THE DEPENDENCE BETWEEN THE CONDUCTIVITY AND THE TEMPERATURE CHANGES FAIRLY CLOSELY RESEMBLES THE SIMILAR DIAGRAMS FOR SEMICONDUCTORS. IT WAS CONCLUDED THAT THE GREATER RELATIVE PERMITTIVITY OF Na–MONTMORILLONITE IS DUE TO THE DIFFERENCE IN DISSOCIATIVE CAPACITY OF Na AND Ca CATIONS.

Introduction

Montmorillonites are anisodimensional plate–like particles which have an aluminosilicate network layer structure. Certain layers have a plane sheet structure: between two SiO_4 tetrahedral sheets there is an octahedral sheet consisting of $Al(O,OH)_6$ groups, linked by mutual oxygen atoms. It is presumed that the Al^{3+} partly replaces the Si^{4+}; the Al^{3+} can partly be replaced by Fe^{2+} or Mg^{2+}. Thus, in the triple layer complex there is always an excess of negative charge and, to compensate this, cations which can be exchanged by other cations (e.g. Na^+, Ca^{2+}, Mg^{2+}, H^+, etc.) occupy the space between the layers [1].

In the anhydrous state, the distance between the layers is 0.96 nm; in the case of complete hydration, however, the mineral can freely swell because of the small

layer–charge between the layers, which makes the internal and external surfaces free. Then depending on the nature of the cations, the interlayer distance increases from 2.0 to 5.0 nm. It is possible that a positive charge double layer is formed on the edges of the plates, due to the falling–off of tetrahedral silicate and octahedral aluminate layers. The capacity of montmorillonites for low anion–exchange can be explained by the presumed formation of positively charged double layers.

The nature and quantity of the attached ions determine the surface charge, the surface potential and the active adhesive forces of montmorillonite particles, which decisively influence the swelling ability , the possibility of peptization and the rheological properties [2,3].

During our examinations, we applied various monocationic montmorillonites as dielectrics and sought a connection between the physical–chemical and dielectric properties.

The aim of these examinations was essentially to improve the effects of the factors determining the corrosive aggressivity of the soil in the underground metallic structures by determining the typical dielectric properties of clay minerals, *i.e.* the colloid inorganic components of the soil.

Materials and methods

The crude bentonite used was from a mine at Mád. The colloid fraction obtained after peptization and fractionation contained only montmorillonites [4]. Peptization was performed with Na_2CO_3 and Na_3PO_4, which yielded the Na,Ca–montmorillonites. The montmorillonites (peptized by Na_2CO_3) which contained two kinds of cations were treated later with NaCl or $CaCl_2$ to produce Na– and Ca–montmorillonites [5].

From various samples we made tablets at 500 bar and dried these at 100 °C (373 K) until they showed conductivity saturation (G = const.). In order to ensure that the humidity was constant and typical for the given sample the measurements were made at an

equilibrated air humidity, which was determined with silica gel.

The tablets were placed between miniature condensing armatures and used as an element of an AC bridge. The capacitance and conductivity of the capacitor were measured as functions of temperature. Next the values of the relative permittivity (ϵ_r) were calculated. This method was described earlier [6].

Results and discussion

Typical data on the examined samples are shown in Table I. For the first three, there was no significant difference in the dry sample as concerned the distance between the plane sheets, measured by X–ray diffraction, or from the point of swelling. In an aqueous

Table I

Sample notation	Sample	Plane sheet distance d_{001} nm	Sediment vol. cm^3 Dose:1g substance in $10cm^3$ water
K1	Na,Ca–montmorillonite obtained by Na_3PO_4 peptization	1.265	stable suspension
K2	Na,Ca–montmorillonite obtained by Na_2CO_3 peptization	1.263	stable suspension
K3	Na–montmorillonite	1.228	stable suspension
K4	Ca–montmorillonite	1.426	3.7

medium a stable suspension is formed, and therefore no measurable sedimentation is present.

The dissociation of montmorillonites is determined by how strongly the

exchangeable cations are bound to the surface of the particles. The strength of the cation bond is determined by its valency and by the rule of the lyotropic series. Hence, in the dissociation of Ca–montmorillonite it is smaller than that of a Na–montmorillonite, and it is understandable that a Ca–montmorillonite does not swell in water so well, does not peptize and has a small volume of sedimentation (Table I).

The relative permittivity of various samples was measured as a function of temperature and the results are shown in Fig. 1. The samples treated with various Na^+ salts display almost the same behaviour; the only difference is the typical phase–change temperature.

All four samples have a very significant relative permittivity coefficient. As the temperature rises, the curves diverge more and more, which relates to the conclusion that the dipole moment is determined by some other induced polarization of equalizing ions.

In the presence of the same equalizing cations (samples K1 and K2) the permittivity is a function of number of exchangeable anions on the edges. Taking into consideration the van OLPHEN theory [3] about the positive double layer, the behaviour of the two dielectrics can be explained. Due to the interaction of the two dissimilar types of double layer, the molecules polarize differently. By examining the natures of cations in exchangeable positions (samples K3 and K4), it is obvious that the Na^+ ion, with high polarizability, predominates relative to the effects of the Ca^{2+} ion in Ca–montmorillonites. Samples K1 and K2 and samples K3 and K4 show similar dielectric behaviour, which is obvious from the $tg\delta$ vs. temperature diagrams in Fig. 2.

Figure 2 reveals that the behaviour of samples K1 and K2 differs significantly from that of samples K3 and K4. The ϵ_r vs. T diagrams of samples K1 and K2 (Fig. 1) show a phase change which can be seen in Fig. 2 as $tg\delta$ peaks. The phase–change temperature for sample K1 is –16 °C (257 K), while that for sample K2 is –22 °C (251 K). This means that the activation energy of sample K2 is smaller than that of sample K1. It also means that the "freezing" of different ions ceases. The course of the $tg\delta$ vs. T curve relates to a further

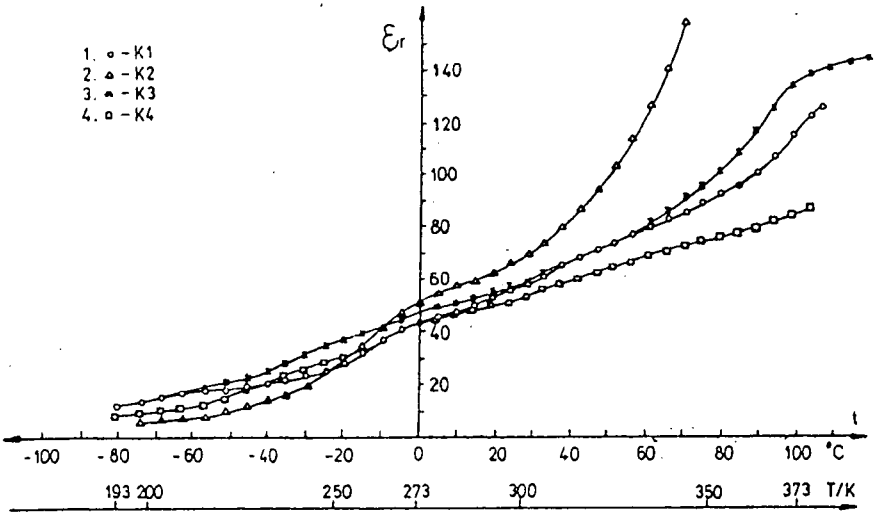

Figure 1: Relative permittivity of modified montmorillonites as a function of temperature

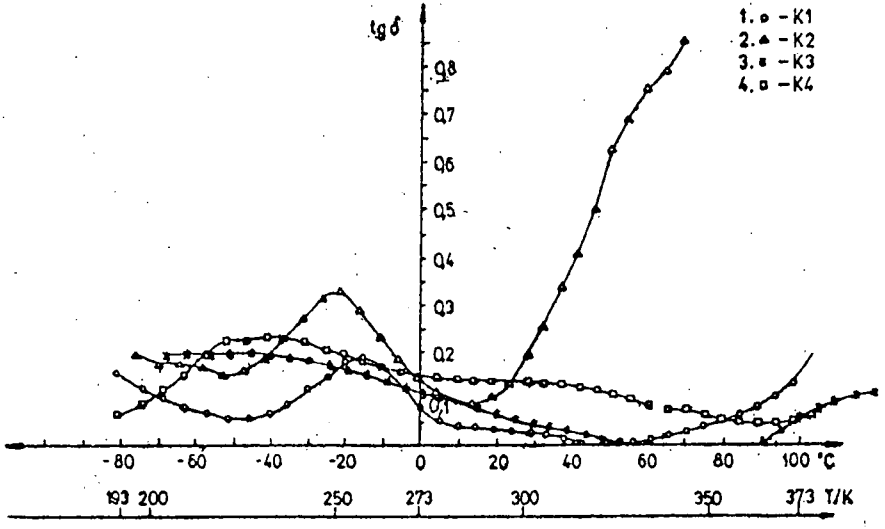

Figure 2: Dielectric loss of modified montmorillonites as a function of temperature

two "freezings" or "meltings". The characteristic rise in tgδ begins at 100 °C (373 K) for sample K2, whereas for sample K1 the tendency to a strong rise begins at 30 °C (303 K). The tgδ vs. T diagrams for monocationic Na–montmorillonites (K3) at –60 °C (213 K), and for Ca–montmorillonites (K2) at –45 °C (228 K), also show the phase change, but the further course of the curves is very different from the previous one.

Further, changes in specific conductivity (κ) as a function of temperature (logκ vs. 1/T) were tested (Fig. 3). The dielectric losses reveal that samples K1 and K2, and also samples K3 and K4, exhibit mutual similarity; this is clearly illustrated by the logκ vs. 1/T curves. Two typical plots are presented in Fig. 3. The plots for samples K1 and K2 comprise two linear sections their starting points being at the same temperature; the

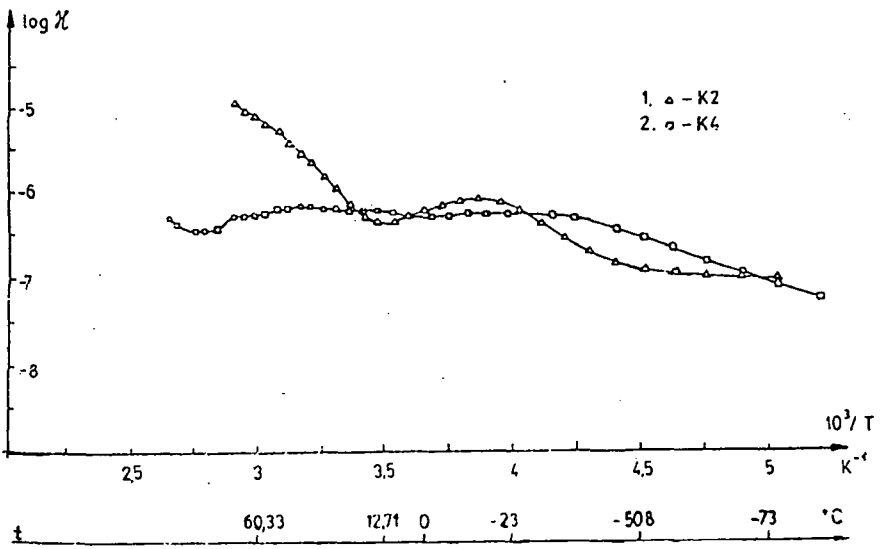

Figure 3: Dependence of logarithm of specific conductivity of modified montmorillonites on reciprocal absolute temperature

dielectric losses showed the maximum. The course of the curves is reminiscent of the similar curves (logγ vs. 1/T) for impure semiconductors [7]. It is assumed that these linear dependences originate from the increase in the number of dominant charge carriers with

temperature rise (resulting also in an increase in the specific conductivity). In contrast, the diagrams for monocationic montmorillonites (samples K3 and K4; Fig. 3 shows the diagram for sample K4) in the temperature interval from –40 °C to 40 °C the specific conductivity remains practically constant. The results obtained so far permit the conclusion that the relative permittivities of sample K1 and K2 (which are models of the montmorillonites in basic soils) are complex functions of the thickness of the negative double layers on the surfaces and the positive electric double layers on the edges. As the negatively charged networks are compensated by the same cations (Na,Ca–montmorillonite), the higher relative permittivity of sample K2 is attributed to the higher polarizability of the CO_3^{2-} ions in the exchange position on the edges of the network. If it is accepted that the dissociability of cations in the exchange position causes swelling and the possibility of peptization, and also influences zeta–potential (this determines the dipole moment of particles), then it is possible that the dissociability decreases the relative permittivities of Ca–montmorillonites relative to those of Na–montmorillonites.

To summarize, it is concluded that the dielectric characteristics of montmorillonites are function of the activities of the anions and cations in the system. The relative permittivities of the tested samples are relatively high (ϵ_r = 40–60 between –10 and +30 °C) and should therefore be taken into consideration in an evaluation of the corrosive aggressivity.

References

[1] *Nemecz, E.*: Agyagásványok, Akadémiai Kiadó, Budapest (1973).

[2] *Szántó, F.*: Földtani Közlöny 93. 142 (1963).

[3] *Olphen van, H.*: An Introduction to Clay Colloid Chemistry, Chap. 7., Int. Sci. Publ. John Wiley, New York (1963).

[4] *Szántó, F., M. Gilde-Farkas, B. Várkonyi, J. Balázs*: Acta Geol. Acad. Sci. Hung. 11, 409 (1967).

[5] *Patzkó, Á., P. Szántó:* 5th Meeting of European Clay Groups, Prague, 1983. Charles University (1985).

[6] *Koczó, F., M. Dulic, L. Horváth:* Acta Phys. et Chem. (Szeged) 30, 141 (1984).

[7] *Solymar, L., D. Walsh:* Szilárdtestek elektromos tulajdonságai, Műszaki Kiadó, Budapest (1972).

[8] *Borbély, M.:* Magistarski rad, Technoloski fakultet, Novi Sad (1975).

ДИЭЛЕКТРИЧЕСКИЕ СВОЙСТВА МОНОКАТИОНИТНЫХ МОНТМОРИЛЛОНИТОВ

Ф. КОЦО, А. ПАЦКО, И. БОРБЕЛЬ

Исследованы диелектрические свойства натриевого, кальциевого и смешанного натро–кальциевого монтморрилонитов и сопоставлены с их набухающей спасобностью и рентгено–структурными данными. Диэлектрические измерения проводились в зависимисти от температуры при постоянных частотах. Показано, что свойства образцов зависят в первую очередь от природы и способа связывания обменных катионов, а во вторую – от анионов, образующих двойной электрический слой на гранях минералных частиц. Температурная зависиность проводимости исследуемых монтмориллонитов соответствует в основном аналогичным зависимостям для полупроводников. Большая проводимость натриевных монтмориллонитов по сравнению с кальциевыми, обусловлена большей обменной емкостью натриевых ионов.